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FOAM GLASS FROM MECHANOACTIVATED ZEOLITE-POOR ROCK

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The possibility of making foam glass from zeolite-poor rock is examined. Mechanoactivation of the crushed rock or the addition of opoka rock to alkaline zeolite-containing compositions significantly increases the foaming intensity. In addition the macro- and microporous structure of the foam material obtained from rock conventionally crushed in a rod mill differs from that of the foam material made from mechanically activated rock powder.

Key words: foam glass, zeolite-containing rock, mechanoactivation, melting, pore formation.

Different forms of natural raw material are now being examined for making foamed materials such as foam glass by means of energy-conserving technology without making glass beforehand. Such porous construction materials are sometimes designated by the general term 'foam silicates'. Siliceous rock — opoka, trepel and diatomite — is used as the silicate raw material for making foam silicates [1 – 3]. Zeolite tuffs are the most suitable aluminum-silicate raw materials [3 – 5]. Zeolitic rocks (ZR) are attractive for making foam silicates because some zeolites are capable of thermally activated foaming at their natural melting temperature. The word zeolite comes from the Greek for 'boiling stone'. The pore-formation of zeolites is associated with a complex thermal transformation of zeolitic water; the mechanism is determined by the form and valence of the intracrystalline cations in these minerals [6 – 8]. Since the sources of the foaming gas in ZR are zeolite-group minerals, the foaming intensity depends directly on their concentration in tuff. Tuffs with zeolite content > 40% are characterized, as a rule, by a high foaming ratio in alkaline compositions in the temperature range 750 – 850°C. In Russia deposits of high-zeolite rocks are found in Siberia and the Far East. The deposits in the European part of Russia are predominately poor (zeolitization about 20%). For zeolite-poor rocks the foaming intensity depends on many factors such as the type of zeolitization (hidden or open), the general chemical composition of the raw material, the mineral composition of the surrounding rock and others.

Since their low content of zeolites, zeolite-poor rocks cannot be used directly as molecular sieves, desiccants, sorbents and so forth. A promising application of such mineral raw material is in construction, including in the production of thermal insulation and heat-insulating porous structural materials. However, in many cases low-zeolite raw material requires additional mechanoactivation of the rock or enrichment with zeolites, which increases the foamability of the rock [9]. The foamability of the compositions can also be increased on basis on such raw materials by complicating the raw base with materials which are sources of the foaming gas. We shall examine the results of an investigation of the application of low-zeolitization minerals for making foamed silicates.

METHODS OF STUDY AND ROCK CHARACTERISTICS

The following methods were used: x-ray fluorescence for chemical analysis of the rocks (VRA-20R x-ray Analyzer), powder x-ray diffractometry for mineral analysis of the initial raw material and intermediate products (Thermo Scientific ARL-X'tra diffractometer; CuK_α radiation; regime: 40 kV, 40 mA) together with the PDF-4 database and scanning electron microscopy (Philips XL30-FEG). A Microtras X100 particle-size analyzer was used for granulometric analysis of the powders.

Zeolite-containing rock from the Tatarsko-Shatrashanskoe deposit (Tatarstan) with zeolite content in the 15%[4] range served as the starting raw material. This mineral raw

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[4] Here and below, the content by weight, %, unless stipulated otherwise.

TABLE 1. Chemical Composition of Zeolite-Containing Rock from the Tatarsko-Shatrashanskoe Deposit

Oxides content, wt.%, in dry material										
SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Other
64.76	4.62	0.22	1.42	0.01	1.72	13.26	0.09	0.81	0.07	13.77

material is distinguished by its high concentration of calcite, a mineral component of rock that is unfavorable for the formation of inorganic foam. CaO, which forms after thermal decomposition of calcite, sharply lowers the viscosity of melt, as a result of which the foam formed during the fabrication of foamed silicates becomes unstable. The chemical composition of the rock is presented in Table 1.

The mineral components of the rock are as follows (%): opal-cristobalite-tridimite phase — OCT (42), calcite (21), zeolite — heulandite-clinoptilolite (15), quartz (< 5), feldspar (< 5) and clayey materials (17). The powder diffraction profile of ZR is shown in Fig. 1. Electron microscopy shows that the zeolites in the rock are represented by a hidden crystalline form, i.e., the zeolite crystals are included in dense growths of other mineral components and do no manifest in the chip surfaces of the rock under magnification.

The rock was crushed in a rod mill. The powder obtained served as the initial material for the investigation and is designated in the text as ZR_{ini}. The mechanoactivation of ZR_{ini} was performed in air in steel drums in a M-3 centrifugal-planetary mill with grinding-crushing action. The activation times were 2 and 5 min. The disperse composition of ZR_{ini} and the powders after mechanoactivation is presented in Table 2.

To increase the source of the foaming gas in ZR_{ini}-based compositions crushed siliceous rock — opoka from the Shipovskoe deposit (Kazakhstan) — was added in the amounts 10, 20 and 30%. For augmentation of the zeolite-containing raw material opoka was chosen because its main mineral component is highly reactive amorphous silica, which when wetted with a sodium hydroxide solution forms sodium polysilicates — the source of the foaming gases (water vapor) in the region of the pyroplastic state of the opoka composition. Aside from amorphous silica opoka also contains quartz, cristobalite and clayey minerals [3].

Thermally activated pore formation in low-zeolite rock was accomplished in compositions containing 20% NaOH.

The powders were wetted with a water solution of sodium hydroxide to the molding moisture content and granules were formed, dried and annealed in the temperature range 700 – 900°C with 10-min soaking at each temperature. The intensity of the pore formation was determined according to the post-annealing density of the granules.

RESULTS AND DISCUSSION

It is well known that in tuffs with zeolitization of the open-crystalline type, for example, in tuffs in the Shivyrtuiskoe deposit, at least 50% amorphization of clinoptilolite is observed after 5 min of mechanoactivation in a planetary mill [10]. It is the amorphization of the crystalline phases that is thought to increase the chemical activity of mechanoactivated powders of zeolitized tuffs. In the case of mechanoactivation of rock with the hidden crystalline form of zeolitization the clinoptilolite and other glass-forming components (OCT phase, quartz) are not subjected to significant structural changes. The diagnostic reflections of clinoptilolite ($d = 8.931$ and 7.907 Å) as well as reflections of the OCT phase and quartz remain unchanged after 2- and 5-min activation. Amorphization is observed only in calcite, and it is manifested as an approximately 1/3-fold reduction of the intensity of the diagnostic reflections at $d = 2.84$ and 2.496 Å after 5-min mechanoactivation (Fig. 1).

Nevertheless, a significant increase in the intensity of pore formation is observed in mechanoactivated powders (Fig. 2). The partial amorphization of calcite after 5-min activation does not explain the increase of pore formation in activated powders, especially since the intensity of this process is practically identical after 2- and 5-min activation.

After 2-min activation the granulometric composition of the powder shifts into the fine-dispersion region. For longer activation times the powder grains grow larger; this is associated with the well-known phenomenon of agglomeration of fine powders (see Table 2). The increase of the dispersity of

TABLE 2. Content of Particles of Different Size versus the Conditions of Dispersion of ZR

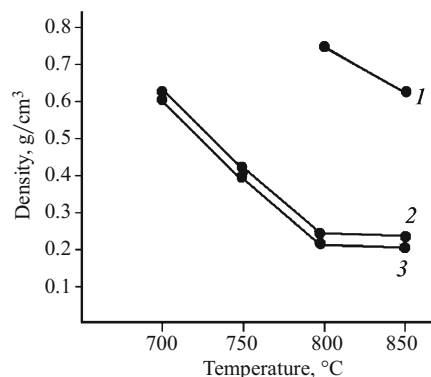| Dispersion conditions	Particle size, μm				
	< 5	$5 – 10$	$10 – 50$	$50 – 100$	> 100
Activation time:	Particle content, %				
5 min	16.62	9.59	44.66	15.99	13.14
2 min	28.36	17.78	47.68	5.14	1.04
Initial powder	8.49	5.06	27.83	24.99	33.63
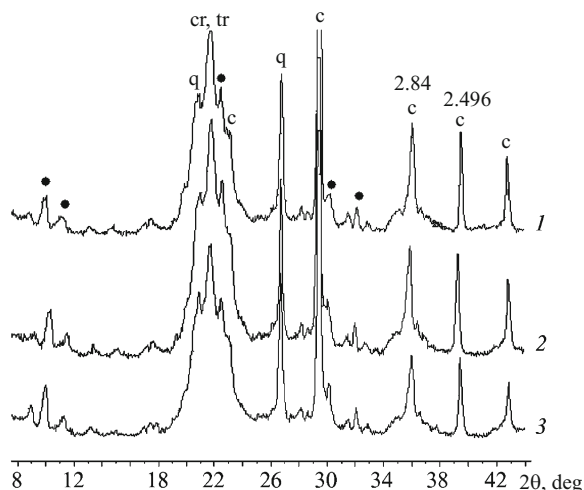
Fig. 1. Diffraction profiles of ZR from the Tatarsko-Shatrashanskoe deposit: *1*) initial rock; *2*) after 2-min mechanoactivation; *3*) after 5-min mechanoactivation; ●) clinoptilolite; q) quartz; cr) cristobalite; tr) tridimite; c) calcite.

Fig. 2. Temperature variation of the density of the granules fabricated from compositions based on powder of the initial ZR (*1*), ZR powder mechanoactivated for 2 min (*2*) and ZR powder mechanoactivated for 5 min (*3*).

the powder undoubtedly influences the reactivity of its components, which can lower the sintering temperature of the granules. However, this cannot explain the intense pore formation for granules fabricated from activated powders. A reduction of the sintering and melting temperatures of the granules of ZR_{ini} powder owing to a 25% increase in the sodium hydroxide composition likewise changes the intensity of foaming. With good fusing of the granules the foaming was negligible, just as with 20% NaOH. It is known that the main condition for the formation of foam glass is that the two processes — melting of the composition and release of a gas phase in the fused micropores — must coincide in time. Weak pore formation with good fusing of the granules indicates that there is no source of foaming gas in the source or the two processes do not coincide.

Mechanoactivation of the ZR_{ini} powder not only increases the foaming intensity but it also breaks up dry granules into fragments under room conditions even before annealing. Granules prepared from ZR_{ini} do not break up into fragments.

In a previous investigation of pore formation in alkaline compositions with highly zeolitized tuff the granules broke up into fragments when powder of raw material was used without mechanoactivation. Dry granules breakup because NaOH in granules interacts with CO_2 and H_2O molecules in the air with carbonate compounds — trona $(Na_3[CO_3][HCO_3] \cdot 2H_2O)$ — being formed. Trona manifests as filamentous and needle molecules, emerging from the pores in a dense matrix, on the chipped faces of fractured granules [3].

These two processes — a significant increase in the intensity of foaming and carbonatization of alkali in granules with activated powder of the rock with the same concentration of zeolites in all samples — attests that mechanoacti-

vation results in fracture of mineral growths and release of zeolites in a free state. These studies suggest that the initial idea of zeolites not affecting the carbonatization of sodium hydroxide in dry granules is wrong. It is known that zeolites sorb many gases, including carbon dioxide from air, and catalyze chemical reactions [11]. Probably, as a result of being released from dense mineral growths the zeolites start to manifest their own specific qualities, which is what leads to the carbonatization of NaOH in granules that is typical for zeolite-alkaline compositions.

The intensification of the foaming of activated ZR powders is also associated with the breakup of mineral growths and release of zeolites from them. The sources of the foaming gas — water vapor in ZR — are water-containing zeolitic minerals. However, under ordinary conditions the zeolitic water of heulandite-clinoptilolite is completely removed during the amorphization of zeolites in the temperature range 300 – 600°C, i.e., to melting of the composition. The source of foaming gas in the channels of zeolites can be partially preserved up to the working temperature of foamed silicate manufacture (700 – 850°C) by means of occlusion by intracrystalline channels and voids in zeolites of alkaline-group elements. This is accomplished by wetting powder with a sodium hydroxide solution. Probably, for the hidden crystalline form of zeolitization of the rock, especially with low concentrations of this material, the zeolites in dense growths are inaccessible to the NaOH solution, and for this reason the gas phase in them is largely removed before the melting temperature of the granules is reached.

The results of these studies show that when zeolite-containing rock is used as a raw material the particulars of the type of zeolitization of tuff must be taken into account. For successful manufacture of foamed silicates from low-zeolite tuffs with zeolitization of the hidden crystalline form brief activation of the powders (first few minutes) is required; this results only in the fracture of mineral growths without amorphization of the zeolites.
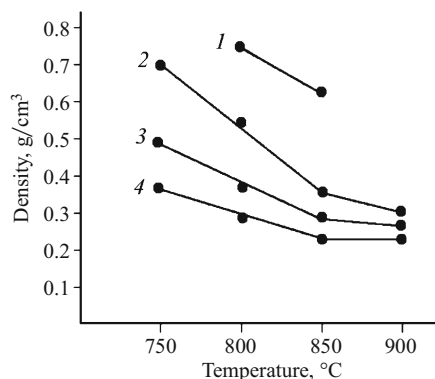
Fig. 3. Temperature variation of the density of granules fabricated from the following compositions (wt.%): *1*) Zr_{ini} — 80; NaOH — 20; *2*) ZR_{ini} — 70; opoka — 10; NaOH — 20; *3*) ZR_{ini} — 60; opoka — 20; NaOH — 20; *4*) ZR_{ini} — 50; opoka — 30; NaOH — 20.

Fig. 4. Micro- and macrostructure of foamed silicate fabricated from zeolite-carbonate rock: *a*) mechanoactivated raw material; *b*) with the addition of 30% opoka.

As shown above, the composition ZR_{ini} + NaOH does not foam up in the temperature range 700 – 850°C. When siliceous rock, forming under alkaline conditions a source of the foaming gas phase — hydrated sodium polysilicates, is added to such a composition the intensity of the foaming increases. The density of granules after annealing with the addition of 10, 20 and 30% comminuted opoka to the composition ZR_{ini} + NaOH is presented in Fig. 3.

The direct dependence of the foaming intensity of the granules on their opoka content naturally follows from the increase of the content of hydrated sodium polysilicates, formed on interaction of amorphous opoka with the NaOH solution, in alkaline compositions. When up to 30% opoka is added to the composition the foaming intensity is comparable to that of the compositions made from mechanoactivated powders. However, the micro- and macrostructure of foamed silicates, made from mechanoactivated zeolite powder, differs from that of the zeolite-opoka composition (Fig. 4).

The enclosing walls of the pores in foamed silicates made from mechanoactivated powder are densely permeated with micro-openings. This state of the enclosing walls of macropores can be regarded as intermediate between closed and open pores. It is well known that foamed glass with open porosity is characterized by higher values of the acoustic insulation. Acoustic foamed glass is manufactured from compositions with elevated CaO content in the batch, which is accomplished by introducing carbonates into them [12]. However, the enhancement of the acoustic properties of foamed materials due to the formation of open porosity results in a reduction of the strength. Foamed silicate obtained from zeolite-containing raw material with a high native content of calcites is an excellent raw material for fabricating high-strength acoustic foamed silicate. This is accomplished by the fact that the walls of the pores do not rupture completely, but rather they become covered with numerous micro-openings because the viscosity of the melt is low. The pseudo-open porosity imparts strength under compression comparable to that of ordinary foam glass [13].
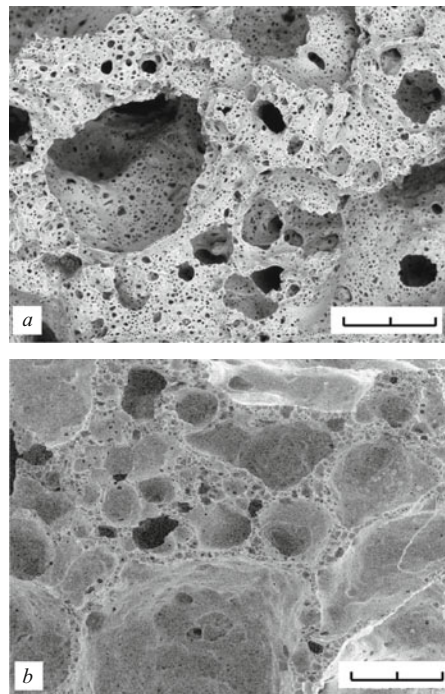
The results of the present investigations show that the typical technological production schemes and typical compositions cannot be applied to zeolite-containing raw materials. When zeolite-containing raw material is used for fabrication of foam silicates an individual approach taking account of the structural-mineralogical-chemical particulars of the rock found in each deposit must be used. Taking account of the particulars low-zeolite rock with hidden crystalline zeolitization can be a completely satisfactory raw material for the production of foamed silicates.

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